

# A truth about Brownian motion in gases and in general

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Real thermal motion of gas molecules, free electrons, etc., at long time intervals (much greater than mean free-flight time) possesses, contrary to its popular mathematical models, essentially non-Gaussian statistics. A simple proof of this statement is suggested basing on only the determinism and reversibility of microscopic dynamics and besides incidentally derived virial expansion of a path probability distribution of molecular Brownian particle.

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1. Thermal chaotic Brownian motion of particles of the matter is mechanism of diffusion as well as many other transport processes. It is interesting by itself too, since statistics of random walk of test or marked “Brownian” particles contains complete information about transport process as a whole including its noise and fluctuations. In spite of this, dynamical theory of molecular Brownian motion remains almost undeveloped. Apparently, the common opinion is that anyway it should confirm the well known beautiful probability-theoretic scheme based on the celebrated “law of large numbers” [1] which foretells that at sufficiently large spatio-temporal scales probability density of displacement, or path,  $\Delta \mathbf{R}$ , of a Brownian particle (BP) during time  $t$  has universal form of the Gaussian distribution. For symmetric 3-D random walk that is

$$V_G(t, \Delta \mathbf{R}) = (4\pi Dt)^{-3/2} \exp(-\Delta \mathbf{R}^2/4Dt) .$$

In fact, it was rigorously proved [2, 3] that such is the asymptotic of chaotic walk of hard ball in so non-random environment as static periodic lattice of scatterers (also hard balls). Seemingly, Brownian motion of gas atoms or molecules all the more can not display something else. Indeed, the Boltzmann-Lorentz equation [4], which comes from the Boltzmann equation when applied to self-diffusion of gas atoms, produces the Gaussian asymptotic. Nevertheless, not all is so simple as seems.

Recall, firstly, that the Boltzmann-Lorentz equation along with the Boltzmann’s one is rather rough model since results from violent truncation of the exact BBGKY hierarchy of equations and its closure with the help of archaic Boltzmann’s “molecular chaos” hypothesis [4, 5, 6]. However, it was pointed out more than once [4, 7] that Boltzmann’s argumentation [8] looks enough convincing only if applied to spatially uniform gas. As to attempts to deduce “molecular chaos” from BBGKY equations themselves, they proved to be unsuccessful [9]. In opposite, it was shown [10] (see also [11, 12]) that reformulation of BBGKY equations in terms of inter-particle “collisions” (instead of continuous interactions) leads to equations which are evidently incompatible with this hypothesis if a gas is spatially nonuniform. In other words, the very

fact of participation of particles in the same collision (or connected conglomerate of collisions) at indicated place is sufficient reason for mutual statistical dependence of the particles. At the same time, if wishing to consider displacement of BP (test particle) one has to localize its initial position and thereby disturb uniformity (translational invariance) of infinitely many distribution functions (DF) what describe BP under its interactions with gas. Consequently, after all one has to deal with an infinite chain of equations. Attempts to construct approximate solutions to them were made in works [10] (see also [11]) and [12]. Their findings, of course, qualitatively differ from the Gaussian asymptotic (but qualitatively confirm the early phenomenological theory [13, 14, 15]).

Secondly, Gaussian asymptotic of the ball’s walk in static lattice is closely connected with its ergodicity [2, 3, 16]: results of time averaging over  $n \rightarrow \infty$  fragments of its trajectory (with each fragment consisting of free flight and collision) almost surely are independent on the trajectory. This is possible due to the fact that any trajectory is fully determined by its single fragment (e.g. initial one), and a ratio of number,  $d = 5n$ , of quantities describing the trajectory to number,  $p = 5$ , of its specifying parameters is unrestrictedly large,  $d/p \rightarrow \infty$ . But a (weakly non-ideal) gas is quite another matter. Here any trajectory of Brownian (test) particle is made of  $n \approx t/\tau$  similar fragments, with  $t$  being observation time and  $\tau$  mean free flight time, and is exhaustively characterized by  $d = 6n$  quantities. However, it is specified by not only initial state of the particle under consideration but also initial states of many other particles. It is easy to see [12] that a number  $m$  of such particles grows with time by far faster than  $n$ , so that  $n/m \rightarrow 0$ . Thus now the ratio of number of quantities what completely describe all details of a trajectory to number,  $p = 6m$ , of parameters (initial conditions) what determine these details, tends to zero,  $d/p \rightarrow 0$ , as contrasted with above case. By this reason, hardly results of time averaging (for instance, “diffusivity” or “collision probabilities”) will turn out to have “almost sure” same limits for different trajectories. Here are no grounds for ergodicity, the “law of large numbers” (which needs in beforehand prescribed “collision probabilities” [1, 11, 17]) and Gaussian asymptotic. Even in finite gas of  $N < \infty$  particles (in box or torus) necessary grounds for ergodicity arise not earlier than after time

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$> N\tau$  [12]. This gives illustration of footnote remark in [16] that a value of ergodicity in physics looks overestimated since limit  $N \rightarrow \infty$  is much more important for physics than limit  $t \rightarrow \infty$ . Besides, in essence, such warning was highlighted already by N. Krylov [18].

In principle, similar reasonings [11, 15, 19, 20], as well as BBGKY equations or their analogues, are applicable to any realistic many-particle system, and therefore particular case of gas has general physical significance. But BBGKY equations yet are so bad investigated that none supplementary tools would be superfluous. Below, basing on determinism and reversibility of microscopic dynamics only, we will derive a kind of virial expansion for true probability distribution of the BP's displacement,  $V_0(t, \Delta \mathbf{R})$ . Then connect coefficients of this expansion with joint correlation functions of BP and gas and with usual joint DF. Finally, show that all these taken together imply a differential inequality for  $V_0(t, \Delta \mathbf{R})$  which definitely forbids Gaussian asymptotic of  $V_0(t, \Delta \mathbf{R})$  (but allows for non-Gaussian distribution obtained in [12] by approximative solving BGKY equations).

2. Let a gas of  $N \gg 1$  atoms in volume  $\Omega$  contains a "Brownian particle" (BP). Consider, under the thermodynamical limit  $N \rightarrow \infty$ ,  $\Omega \rightarrow \infty$ ,  $N/\Omega = \nu_0 = \text{const}$ , statistical ensemble of phase trajectories of this system which responds to canonical equilibrium distribution of its initial state at  $t = 0$ , supposing that at  $t > 0$  BP is subjected to constant external force  $\mathbf{f}$ . Time reversibility of phase trajectories implies many relations between statistical characteristics of their ensemble [21, 22, 23]. In particular, according to [21] one can write

$$\langle A(\mathbf{q}(t))B(\mathbf{q}(0))e^{-\mathcal{E}(t)/T} \rangle = \langle B(\mathbf{q}(t))A(\mathbf{q}(0)) \rangle \quad (1)$$

Here brackets  $\langle \dots \rangle$  designate ensemble averaging,  $\mathbf{q}(0) = \mathbf{q} = \{\mathbf{R}, \mathbf{r}_1, \dots, \mathbf{r}_N\}$  are space coordinates of BP and atoms,  $\mathcal{E}(t) = \mathbf{f} \cdot [\mathbf{R}(t) - \mathbf{R}(0)]$  is work made by the external force during time interval  $t$ ,  $A(\mathbf{q})$  and  $B(\mathbf{q})$  are "arbitrary functions", and  $T$  is initial temperature of the system. This equality holds also when BP has internal degrees of freedom.

Let  $B(\mathbf{q}) = \Omega \delta(\mathbf{R} - \mathbf{R}_0) \exp[-\sum_j U(\mathbf{r}_j)/T]$  and  $A(\mathbf{q}) = \delta(\mathbf{R} - \mathbf{R}')$ . Then r.h.s. in (1) takes form

$$\langle B(\mathbf{q}(t))A(\mathbf{q}) \rangle = \mathcal{F}\{t, \mathbf{R}_0, \phi|\mathbf{R}'\} \equiv V_0(t, \mathbf{R}_0 - \mathbf{R}') + \sum_{n=1}^{\infty} (\nu_0^n/n!) \int^n F_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}') \prod_{j=1}^n \phi(\mathbf{r}_j),$$

where  $\phi(\mathbf{r}) = \exp[-U(\mathbf{r})/T] - 1$ , symbol  $\int^n$  means integration over  $\mathbf{r}_1 \dots \mathbf{r}_n$ , function  $V_0(t, \mathbf{R}_0 - \mathbf{R}')$  is probability density of finding BP at  $t \geq 0$  at point  $\mathbf{R}_0$ , and  $F_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}')$  probability density of this event and simultaneously finding some atoms at points  $\mathbf{r}_j$ , under condition that BP had started from point  $\mathbf{R}'$ . Clearly,  $V_0(0, \mathbf{r}) = \delta(\mathbf{r})$ ,  $\int V_0(t, \mathbf{r}) d\mathbf{r} = 1$ , and

$$\begin{aligned} F_n(0, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}') &= \delta(\mathbf{R}_0 - \mathbf{R}') F_n^{(eq)}(\mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}_0), \\ \mathcal{F}\{0, \mathbf{R}_0, \phi|\mathbf{R}'\} &= \delta(\mathbf{R}_0 - \mathbf{R}') \mathcal{F}^{(eq)}\{\phi|\mathbf{R}_0\}, \\ \mathcal{F}^{(eq)}\{\phi|\mathbf{R}_0\} &\equiv 1 + \\ &+ \sum_{n=1}^{\infty} (\nu_0^n/n!) \int^n F_n^{(eq)}(\mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}_0) \prod_{j=1}^n \phi(\mathbf{r}_j), \end{aligned}$$

where  $F_n^{(eq)}(\mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}_0)$  are equilibrium DF and  $\mathcal{F}^{(eq)}\{\phi|\mathbf{R}_0\}$  their generating functional. In respect to atoms all the DF are normalized as usually [5, 6], that is  $F_n(\dots \mathbf{r}_k \dots |\mathbf{R}') \rightarrow F_{n-1}(\dots \mathbf{r}_{k-1}, \mathbf{r}_{k+1} \dots |\mathbf{R}')$  if  $\mathbf{r}_k \rightarrow \infty$ , and  $F_1^{(eq)}(\mathbf{r}_1|\mathbf{R}') \rightarrow 1$  if  $\mathbf{r}_1 \rightarrow \infty$ . At one this requirement expresses the "principle of decay of correlations".

Initial DF  $F_n(0, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}')$  include all equilibrium correlations between BP and atoms. But any evolution of (ensemble of states of) the system is conjugated with disturbance of detailed balance of collisions and therefore births additional correlations due to joint participation of particles in excess collisions (or "joint nonparticipation" in missing ones). These correlations could be qualified as non-equilibrium ones, but with those reservation that sometimes they describe evolution of not so much a system on its own as our information about it. Traditionally, their contributions to DF are termed "correlation functions" (CF) [4, 5, 6, 24]. Let us designate them as  $V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}')$  and pick out them from  $F_n(t > 0, \dots)$  by definition as follows:

$$\mathcal{F}\{t, \mathbf{R}_0, \phi|\mathbf{R}'\} = \mathcal{F}^{(eq)}\{\phi|\mathbf{R}_0\} [V_0(t, \mathbf{R}_0 - \mathbf{R}') + \sum_{n=1}^{\infty} (\nu_0^n/n!) \int^n V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}') \prod_{j=1}^n \phi(\mathbf{r}_j)]$$

From here it is obvious that  $V_n(0, \dots) = 0$ , and  $V_n(t, \dots) \rightarrow 0$  if at least one of the points  $\mathbf{r}_k \rightarrow \infty$ . In particular,

$$\begin{aligned} F_1(t, \mathbf{R}_0, \mathbf{r}_1|\mathbf{R}') &= \\ &= V_0(t, \mathbf{R}_0 - \mathbf{R}') F_1^{(eq)}(\mathbf{r}_1|\mathbf{R}_0) + V_1(t, \mathbf{R}_0, \mathbf{r}_1|\mathbf{R}'), \end{aligned}$$

where function  $V_1(t, \mathbf{R}_0, \mathbf{r}_1|\mathbf{R}')$  comes from the usual "pair correlation function" [6, 24] in the full two-particle phase space:

$$V_1(t, \mathbf{R}_0, \mathbf{r}_1|\mathbf{R}') = \int \int V_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1|\mathbf{R}') d\mathbf{P}_0 d\mathbf{p}_1 \quad (2)$$

The latter can be connected with the full DF exactly like  $V_1(t, \mathbf{R}_0, \mathbf{r}_1|\mathbf{R}')$  is connected with coordinate ones:

$$\begin{aligned} F_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1|\mathbf{R}') &= V_0(t, \mathbf{R}_0 - \mathbf{R}', \mathbf{P}_0) \times \\ &\times F_1^{(eq)}(\mathbf{r}_1, \mathbf{p}_1|\mathbf{R}_0) + V_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1|\mathbf{R}') \end{aligned} \quad (3)$$

Next, consider left side of (1). Multiply and divide it by  $\langle B(\mathbf{q}) \rangle$  and use the fact that any expression  $\langle \Phi B(\mathbf{q}) \rangle / \langle B(\mathbf{q}) \rangle$ , with  $\Phi$  being some functional of system's phase trajectory, in view of determinism of translation along any concrete trajectory can be interpreted as  $\Phi$ 's average over new ensemble of trajectories induced by new, non-equilibrium, ensemble of initial coordinates and momentums of the system, namely, defined by probability distribution  $\rho(\mathbf{q}, \mathbf{p}) = B(\mathbf{q}) \rho_0(\mathbf{q}, \mathbf{p}) / \langle B(\mathbf{q}) \rangle$ , where  $\rho_0(\mathbf{q}, \mathbf{p})$  denotes original equilibrium distribution. Noticing also that  $\langle B(\mathbf{q}) \rangle = \mathcal{F}^{(eq)}\{\phi|\mathbf{R}_0\}$ , we come to

$$\begin{aligned} \langle A(\mathbf{q}(t))B(\mathbf{q}(0))e^{-\mathcal{E}(t)/T} \rangle &= \\ &= V\{t, \mathbf{R}'|\phi, \mathbf{R}_0\} e^{-\mathbf{f} \cdot [\mathbf{R}' - \mathbf{R}_0]/T} \mathcal{F}^{(eq)}\{\phi|\mathbf{R}_0\}, \end{aligned}$$

where  $V\{t, \mathbf{R}'|\phi, \mathbf{R}_0\}$  is probability density of finding BP at time  $t$  at point  $\mathbf{R}'$  under conditions that initially

it was placed at point  $\mathbf{R}_0$  while the gas was in such perturbed spatially nonuniform non-equilibrium state which would be equilibrium in presence of the potential  $U(\mathbf{r})$ . Mean concentration of atoms in such state equals to

$$\nu\{\mathbf{r}|\phi, \mathbf{R}_0\} = [1 + \phi(\mathbf{r})] \delta \ln \mathcal{F}^{(eq)}\{\phi|\mathbf{R}_0\} / \delta \phi(\mathbf{r})$$

Thus, in total, we arrive at exact relation

$$V\{t, \mathbf{R}'|\phi, \mathbf{R}_0\} e^{-\mathbf{f} \cdot [\mathbf{R}' - \mathbf{R}_0]/T} = V_0(t, \mathbf{R}_0 - \mathbf{R}') + \sum_{n=1}^{\infty} (\nu_0^n/n!) \int^n V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}') \prod_{j=1}^n \phi(\mathbf{r}_j) \quad (4)$$

which connects probability distribution of BP's path in initially non-equilibrium nonuniform gas and analogous distribution, together with generating functional of “non-equilibrium correlations” between previous path of BP and its current environment, for initially equilibrium uniform gas. In case  $\mathbf{f} = 0$ , therefore, r.h.s. represents wholly equilibrium Brownian motion. Notice that similar relation, for perturbed gas density in place of the BP's distribution, was considered in [17].

**3.** To understand benefits of this relation, it is useful to consider it under the formal “Boltzmann-Grad limit” [9] when gas density increases,  $\nu_0 \rightarrow \infty$ , while radii of (short-range repulsive) interactions between BP and atoms,  $r_b$ , and inter-atomic,  $r_a$ , decrease in such way that “gas parameters”  $r_a^3 \nu_0$  and  $r_b^3 \nu_0$  go to zero but mean free paths of atoms,  $\lambda = (\pi r_a^2 \nu_0)^{-1}$ , and mean free path of BP,  $\Lambda = (\pi r_b^2 \nu_0)^{-1}$ , stay fixed. Thus one obtains “ideal weakly-non-ideal gas” where  $F_n^{(eq)} \rightarrow 1$ , in those sense that, for example,  $\nu_0 \int [F_1^{(eq)}(\mathbf{r}_1|\mathbf{R}_0) - 1] d\mathbf{r}_1 \sim \sim \nu_0 r_b^3 \rightarrow 0$ . As the cosequence,

$$\nu\{\mathbf{r}|\phi, \mathbf{R}_0\} \rightarrow \nu_0 [1 + \phi(\mathbf{r})] = \nu_0 \exp[-U(\mathbf{r})/T]$$

This simplification makes it quite obvious that in the Boltzmann-Grad limit on left side of (4) effects of the density perturbation depend on its relative measure  $\phi(\mathbf{r})$  only but not on  $\nu_0$ . Hence, r.h.s. of (4) also depends on  $\phi(\mathbf{r})$  only, that is at any given function  $\phi(\mathbf{r})$  (and fixed  $\Lambda$  and  $\lambda$ ) there exist finite limits

$$\lim \nu_0^n \int^n V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}') \prod_{j=1}^n \phi(\mathbf{r}_j) \neq 0, \infty$$

Moreover, choosing  $\phi(\mathbf{r}) = \phi = \text{const}$  inside sufficiently large sphere (for instance,  $|\mathbf{r} - \mathbf{R}_0| < v_s t_0$  with  $v_s$  being sound speed in our gas and  $t_0 > t$ ), such that a fortiori none correlations go beyond it, we can conclude that (at fixed  $\Lambda$ ,  $\lambda$  and  $t$ ) there exist limits

$$\lim \nu_0^n \int^n V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}') = V_n(t, \mathbf{R}_0 - \mathbf{R}') \quad (5)$$

At that, the gas described by left side of (4) effectively, from the point of view of BP, is spatially uniform at start and what is more during any given time of keeping BP under observation. But its density is  $(1 + \phi)$  times greater than density of the right-hand gas. Correspondingly, (4) takes the form of simple virial expansion:

$$V_0(t, -\Delta\mathbf{R}; 1 + \phi) e^{\mathbf{f} \cdot \Delta\mathbf{R}/T} = \sum_{n=0}^{\infty} \phi^n V_n(t, \Delta\mathbf{R}; 1)/n! \quad (6)$$

Here we introduced  $\Delta\mathbf{R} = \mathbf{R}_0 - \mathbf{R}'$  and third argument representing (dimensionless) gas density measured in units of  $\nu_0$ , so that  $V_n(\dots; 1) = V_n(\dots)$ .

As it follows from (5)-(6), in weakly nonideal gas spatial non-equilibrium correlations do not disappear in relative sense, i.e. if counting upon (elementary volume  $\nu_0^{-1}$  what fall at) one atom, although they disappear in literal sense:  $V_n(t, \mathbf{R}_0, \mathbf{r}_1 \dots \mathbf{r}_n|\mathbf{R}') \rightarrow 0$ .

Let us interpret this statement on the base of those few things what are known about the correlation functions [5, 6, 10, 11, 12, 24], first of all,  $V_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1|\mathbf{R}')$ . In respect to  $\mathbf{r}_1 - \mathbf{R}_0$  this pair CF is nonzero inside a “collision cylinder” having radius  $r_b$  and directed in parallel to relative velocity of the pair of particles (BP and some atom) where absolute vlaue of the CF is comparable with product of one-particle DF, i.e. with first term on r.h.s. of (3). However, the approximative theory [6, 24], conventionally accepted as satisfactory one, says nothing about length of the cylinder. On the other hand, formula (5) clearly prompts that in rigorous theory effective length of collision cylinder is finite and has size of order of  $\Lambda$ . Indeed, let it be  $c_1 \Lambda$ , then volume of the cylinder equals to  $\pi r_b^2 c_1 \Lambda = c_1 \nu_0^{-1}$ , and

$$\int V_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1|\mathbf{R}') d\mathbf{r}_1 = c_1 \nu_0^{-1} \bar{V}_1(t, \Delta\mathbf{R}, \mathbf{P}_0, \mathbf{p}_1), \quad (7)$$

where  $\bar{V}_1(t, \Delta\mathbf{R}, \mathbf{P}_0, \mathbf{p}_1)$  represents mean value of  $V_1(t, \mathbf{R}_0, \mathbf{r}_1, \mathbf{P}_0, \mathbf{p}_1|\mathbf{R}')$  within the cylinder. Combining this expression with (2) and (5), at  $n = 1$ , we make certain of finitness of the limit:

$$V_1(t, \Delta\mathbf{R}) = c_1 \int \bar{V}_1(t, \Delta\mathbf{R}, \mathbf{P}_0, \mathbf{p}_1) d\mathbf{P}_0 d\mathbf{p}_1 \quad (8)$$

At the same time, in literal sense formulas (2) and (8) yield  $V_1(t, \mathbf{R}_0, \mathbf{r}_1|\mathbf{R}') \sim V_1(t, \Delta\mathbf{R}) r_b^2/|\mathbf{r}_1 - \mathbf{R}_0|^2 \sim \nu_0^{-1} V_1(t, \Delta\mathbf{R})/(\Lambda|\mathbf{r}_1 - \mathbf{R}_0|^2) \rightarrow 0$ , since under integration over momentums a very small part of differently oriented collision cylinders only covers (fixed) point  $\mathbf{r}_1$ .

**4.** We have come to curious conclusions.

Operating with coordinate  $\mathbf{r}_1$ , let us average identity (3) over the collision cylinder:

$$\bar{F}_1(t, \Delta\mathbf{R}, \mathbf{P}_0, \mathbf{p}_1) = V_0(t, \Delta\mathbf{R}, \mathbf{P}_0) G^{(eq)}(\mathbf{p}_1) + \bar{V}_1(t, \Delta\mathbf{R}, \mathbf{P}_0, \mathbf{p}_1)$$

Here  $G^{(eq)}(\mathbf{p}_1)$  is the Maxwellian distribution, and the result,  $\bar{F}_1(t, \Delta\mathbf{R}, \mathbf{P}_0, \mathbf{p}_1)$ , can be treated as ensemble average of density of number of two-particle configurations matching up collisions [10]. Then, performing integration over momentums and applying formula (8), we obtain

$$W_1(t, \Delta\mathbf{R}) \equiv \int \bar{F}_1(t, \Delta\mathbf{R}, \mathbf{P}_0, \mathbf{p}_1) d\mathbf{P}_0 d\mathbf{p}_1 = V_0(t, \Delta\mathbf{R}) + c_1^{-1} V_1(t, \Delta\mathbf{R}) \quad (9)$$

For simplicity, confine ourselves by the case  $\mathbf{f} = 0$ . From relation (6) whose both sides in this case concern equilibrium (hence, spherically symmetric) Brownian motion, we can connect  $V_1(t, \Delta\mathbf{R}) = V_1(t, \Delta\mathbf{R}; 1)$  with derivative of the left side by the relative gas density:  $V_1(t, \Delta\mathbf{R}) = [\partial V_0(t, \Delta\mathbf{R}; 1 + \phi)/\partial \phi]_{\phi=0}$ . Then, combining this equality with (9) and noticing that functions  $\bar{F}_1$  and  $W_1$  by their birth from DF  $F_1$  are non-negative, in view of  $W_1 \geq 0$  we come to inequality

$$c_1 V_0(t, \Delta\mathbf{R}; 1) + \left[ \frac{\partial V_0(t, \Delta\mathbf{R}; 1 + \phi)}{\partial \phi} \right]_{\phi=0} \geq 0 \quad (10)$$

Further, let us assume that at  $t \gg \tau = \Lambda/v_0$ , where  $\tau$  is mean free flight time and  $v_0$  characteristic thermal velocity of BP, a probability distribution of BP's path tends to the Gaussian one (see paragraph 1):  $V_0(t, \Delta\mathbf{R}) \rightarrow V_G(t, \Delta\mathbf{R})$ . Besides, take into account that diffusivity of BP,  $D$ , in the Boltzmann-Grad gas is arranged as  $D = \Lambda v_0 = v_0^2 \tau$  and, consequently, together with  $\Lambda$  is inversely proportional to gas density. Therefore left side of (6) should follow from  $V_G(t, \Delta\mathbf{R})$  after change  $\Lambda \rightarrow \Lambda/(1 + \phi)$ ,  $D \rightarrow D/(1 + \phi)$ , that is

$$V_0(t, \Delta\mathbf{R}; 1 + \phi) \rightarrow \left( \frac{1 + \phi}{4\pi Dt} \right)^{3/2} \exp \left[ -(1 + \phi) \frac{\Delta\mathbf{R}^2}{4Dt} \right]$$

Insertion of this expression to inequality (10) yields  $V_G(t, \Delta\mathbf{R}) [c_1 + 3/2 - \Delta\mathbf{R}^2/4Dt] \geq 0$ , i.e. produces obvious contradiction.

Hence, the theory does not allow for the Gaussian asymptotic! This statement, or rather its new proof since it itself is not novell (see paragraph 1), is principal result of the present paper.

Of course, it is not rigorous because we have managed without a concrete definition of the averaging procedure marked by the over-line (though heuristically this is advantage of our consideration). But, in view of (7), this procedure may influence upon numerical value of the coefficient  $c_1$ . This notion, nevertheless, does not spoil our result, since it means merely that we should substitute to (10) minimum of possible values. Our presumption that  $c_1$  is indeed a coefficient, but not a function of  $t, \Delta\mathbf{R}, \mathbf{P}_0$  and  $\mathbf{p}_1$  in (7) or  $t$  and  $\Delta\mathbf{R}$  in (8), also can be justified. Physically, the length of collision cylinder,  $c_1 \Lambda$ , for pair of particles is bounded by collisions with "third particles" which knock out the pair from a number of candidates for collisions. Since the "third particles" originate mainly from uniform background, the constancy of  $c_1$  seems quite natural.

5. In conclusion, a few more remarks.

First, the above formulation of the Boltzmann-Grad limit implied that size of BP is comparable with size of atoms. Therefore conclusions of previous paragraph do not apply to "macroscopic" BP (in respect to it, at least in the limit of infinitely large BP's mass, Gaussian asymptotic remains above suspicion).

Second, and what is allowed for by the inequality (10)? Let  $V_0(t, \Delta\mathbf{R})$  at  $t \gg \tau$  is characterized, similarly to  $V_G(t, \Delta\mathbf{R})$ , by a single parameter, that is diffusivity:  $V_0(t, \Delta\mathbf{R}) \rightarrow (2Dt)^{-3/2} \Psi(\Delta\mathbf{R}^2/2Dt)$ , where  $\int \Psi(\mathbf{a}^2) d\mathbf{a} = 1$ . Then inequality (10) reduces to

$$(c_1 + 3/2)\Psi(x) + x d\Psi(x)/dx \geq 0,$$

thus requiring that function  $\Psi(x)$  must have power-law long tail:  $\Psi(x) \propto x^{-\alpha}$  at  $x \rightarrow \infty$ , where, clearly,  $\alpha \leq c_1 + 3/2$ . But such behavior would lead to unboundedness of higher-order statistical moments of BP's path. Recall, however, that we have once more parameter,  $v_0$ , and hence, at  $t \gg \tau$ , the possibility to write  $V_0(t, \Delta\mathbf{R}) \rightarrow (2Dt)^{-3/2} \Psi(\Delta\mathbf{R}^2/2Dt) \Theta(|\Delta\mathbf{R}|/v_0 t)$ , where  $\Theta(0) = 1$  and  $\Theta(x)$  enough rapidly decreases at infinity. From the point of view of (10), this is also allowed variant. And it reproduces, if take  $c_1 = 2$ , the asymptotic of distribution of BP's path found in [12] in the frame of "collisional approximation" to BBGKY equations [10, 11]. At that, the role of BP was played by test (marked) atom. Such the asymptotic reflects non-ergodicity of its Brownian trajectories, which can be characterized as "flicker" fluctuations of diffusivity (and mobility) of BP [10, 15, 25].

It should be underlined that our present formalism and one exploited in [12] have nothing common among them (except their application). Therefore the remarkable nearness of their results can be rated as evidence for adequacy of both approaches.

At last, thirdly, in our above consideration by the example of pair DF we in fact have outlined connections between the correlation functions, on one hand, and the specific distribution functions (for pair and many-particle collisional configurations) first introduced in [10], on the other hand. In particular, function  $\bar{F}_1$  here is equivalent of function  $A_2$  from [10], while function  $W_1$  defined in (9) is equivalent of  $W_2$  from [12]. Extension of these connections to higher-order DF will unify the two formalisms and, undoubtedly, open new applications of the virial expansions (4) and (6).

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  - [25] The present paper is devoted to 25-th anniversary of first work by me (in collaboration with G. N. Bochkov), [13], on the subjects under consideration.